

Investigations of cathode-electrolyte interfaces by a surface science approach: recent insights from model experiments and analysis of composite electrodes

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The analysis of solid-electrolyte interface (SEI) layers in Li-ion batteries is a challenge. Their buried nature and high reactivity towards ambient atmosphere require sophisticated strategies to access the layers with surface sensitive characterization methods and to analyze them in an unaltered state. In addition, the high compositional complexity of composite electrodes and their surface layers impair the identification of the different phases and render the deduction of reaction mechanisms difficult.

In this contribution, we present our view on surface and interface layer formation in liquid electrolyte cells as obtained from dedicated analysis by photoelectron spectroscopy. In our approach, we use model experiments and reference spectra to support the identification of the different phases and possible reaction schemes. In this way, we accomplish to determine the interfacial electronic structure and to gain insights into the elemental reactions causing electrode surface degradation and surface layer formation.

Our investigations on LiCoO₂ model electrodes indicate that solvent reactions are coupled to catalytic surface activity and that outer sphere solvent oxidation is comparably unlikely. Upon contact to the fully lithiated electrodes, the solvent is reduced and Li semi-carbonates, Li-oxides and Li-fluoride are formed, leading to passivation of the electrode surface. We find that electrode surface degradation occurs only in LiPF₆– electrolyte and not in pure solvent, and attribute the formation of surface degradation (corrosion) layers to the presence of hydrofluoric acid (HF). For LCO composite electrodes cycled in commercial cells, we find that the corrosion layer consists of cobalt oxy-hydroxides, and is covered by a two layer system consisting of an inorganic layer and an organic top layer. At sample positions near the current collector, the SEI thickness is reduced and slightly different in composition than at the electrode surface, which we attribute to different polarization conditions inside the electrode.

In conclusion, our studies highlight the relevance of solvent reduction and catalytic processes for solvent decomposition at liquid electrolyte based cathodes, as well as of chemical reactions for cathode surface degradation. To obtain stable interfaces, contact of solvent and aggressive electrolyte species has to be eliminated.